

EXHIBIT A

Lithium–Quinolate Complexes as Emitter and Interface Materials in Organic Light-Emitting Diodes

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Received February 24, 2000. Revised Manuscript Received April 11, 2000

We synthesized lithium–quinolate complexes, 8-hydroxyquinolinolitolithium (Liq) and 2-methyl-8-hydroxyquinolinolitolithium (LiMeq), as emitter and electron injection/transport materials to be used in conventional two-layer organic light-emitting diodes in combination with *N,N'*-bis(*p*-methoxyphenyl)-*N,N'*-diphenylbenzidine (DMeOTPD) as hole transport material (HTL). The lithium complexes were also examined as interface materials in combination with 8-hydroxyquinolinolato-Al(III) (Alq₃) as emitter material. The device efficiency with these complexes was optimized by combinatorial methods. We also compared the electron injection, transport, and emission properties of Li complexes with the well-known emitter Alq₃ in the same experiment by taking advantage of the combinatorial approach. The Li quinolates are found to be efficient emitter molecules. But the efficiencies of lithium quinolate devices are lower than that of Alq₃ devices. Contrary to the Alq₃ emission, the Li quinolates exhibit a bathochromic shift of emission compared to the respective photoluminescence spectra. No clear evidence of exciplex formation was seen by comparing the photoluminescence spectrum of an equimolar mixture of Li quinolate and DMeOTPD with the observed electroluminescence spectrum. However, the lithium complexes increase the efficiency of an optimized indium–tin oxide (ITO)/DMeOTPD/Alq₃/Al device considerably when used as a thin interface layer between Alq₃ and aluminum. The improvement of device characteristics with lithium quinolates is similar to that obtained with LiF salt.

Introduction

The intensively studied organic light emitting diode (OLED) structure consists of a transparent indium–tin oxide (ITO) anode, one or more organic layers that fulfill the functions of balanced charge injection, transport, and emission, and an aluminum cathode for electron injection. The high work function of aluminum makes it difficult for the low-voltage electroluminescence (EL) applications, though it is a well-known contact material exhibiting good corrosion resistance in silicon integrated circuits. Due to this fact it is necessary to improve the electron injection from the aluminum cathode into the organic layer by interface modification.^{1–4} Hung et al.¹ used a bilayer of Al/LiF as interface to improve the electron injection and to enhance the electroluminescence efficiency. The use of Li metal, as interface between aluminum and the organic layer to lower the driving voltage is also reported.^{5,6} Kido et al.^{2,3} have demonstrated that modification of the Alq₃/Al interface

with either elementary lithium or a lithium compound is caused by elementary doping resulting in the creation of quinolate radical anion, which favors electron injection.^{2,3}

This leads to the question whether the properties of improved electron injection and good electroluminescence efficiency can be realized together in a Li–quinolate complex. Additionally, the effect of lithium–quinolate complexes as interface materials and the comparison with the dielectric LiF is also worth examination. With this idea in mind, we synthesized 8-hydroxyquinolinolitolithium (Liq) and 2-methyl-8-hydroxyquinolinolitolithium (LiMeq) as emitter and interface material to be used in conventional two-layer OLED with *N,N'*-bis(*p*-methoxyphenyl)-*N,N'*-diphenylbenzidine (DMeOTPD) as hole transport material (HTL). Kido et al.³ have reported the use of Liq as interface material in a TPD/Alq₃ device earlier. But the emission properties of these complexes and a systematic comparison with Alq₃ have not yet been reported to the best of our knowledge. The device efficiency with these complexes was optimized by combinatorial methods developed by us and was demonstrated to be efficient and fast in optimization and screening of materials in OLEDs.^{7,8} Furthermore, we compared the electron injection, transport, and emission properties of Li

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complexes with the well-known emitter Alq₃ in OLEDs in the same experiment by taking advantage of the combinatorial approach. Moreover, the effect of lithium complexes as interface materials in ITO/DMeOTPD/Alq₃/Al devices is compared with that of a dielectric like LiF.

Experimental Section

Alq₃ and LiF were purchased from Aldrich and used without any further purification. Dichloromethane was purified and dried according to known procedure.⁹

8-Hydroxyquinolinolitolithium. Liq was synthesized from the dehydration reaction of lithium hydroxide (Merck) and 8-hydroxyquinoline (Aldrich). Dichloromethane was used as solvent. LiOH (0.316 g, 13.2 mmol) and 8-hydroxyquinoline (1.916 g, 13.2 mmol) were added to 40 mL of highly dried dichloromethane in a single-necked flask under an argon atmosphere. The mixture was stirred at room temperature for 24 h. After completion of the reaction, the precipitate was separated by filtration and washed several times with pure dry dichloromethane. The final solid product was dried under high vacuum for 2 days. The product was obtained in 99% yield (1.983 g, 13.1 mmol) as a white powder. ¹H NMR (250 MHz, DMSO) δ (ppm) = 6.75 (d, 1H), 6.90 (d, 1H), 7.28 (t, 1H), 7.38 (dd, 1H), 8.15 (d, 1H), 8.60 (d, 1H); UV-vis (film on quartz, evaporated) λ_{max} = 259 nm; MS (m/z) = 906, 604, 302, 151, 117, 89, 63; FTIR (KBr) (cm⁻¹) = 3044, 1571, 1496, 1466, 1335, 1322, 1106.

2-Methyl-8-hydroxyquinolinolitolithium. LiMeq was synthesized by a similar procedure as described above. LiOH (0.290 g, 12 mmol), and 2-methyl-8-hydroxyquinoline (1.928 g, 12 mmol) (Aldrich) were mixed in 40 mL of dichloromethane. The product was obtained in 98% yield (1.963 g, 11.8 mmol) as a white powder. ¹H NMR (250 MHz, DMSO) δ (ppm) = 6.57 (d, 1H), 6.66 (d, 1H), 7.12 (t, 1H), 7.19 (d, 1H), 7.98 (d, 1H); UV-vis (film on quartz, evaporated): λ_{max} = 259 nm; MS (m/z) = 660, 330, 165, 131, 63; FTIR (KBr) (cm⁻¹) = 3035, 2913, 1589, 1504, 1457, 1371, 1335, 1280, 1103.

Instrumentation. Each of the devices was characterized by measuring current-voltage characteristics with a computerized setup consisting of a luminometer LS100 by Minolta, a multimeter Keithley 2000, and a programmable power supply PN 300 by Grundig. For layer thickness measurements a surface profilometer (Dektak 3030 ST) was used. The thermal characterizations were performed on a TGA (Netzsch STA 409) and DSC 7 (Perkin-Elmer). Cyclic voltammetry measurements were carried out in three-electrode cell with ferrocenium/ferrocene as internal standard and potential assembly from EG&G Princeton Applied Research. UV/vis absorption and fluorescence/electroluminescence spectra were measured on a Hitachi U-3000 UV spectrometer and a Shimadzu RF 5301 PC fluorometer, respectively.

Device Preparation. The devices were measured under ambient conditions in air without any encapsulation against degradation. The comparison of Liq, LiMeq, and Alq₃ was carried out by depositing linear gradients of each of the emitter compounds on top of a layer of DMeOTPD with 50 nm constant thickness on three different substrates in one single experiment. The general device structure for a two-layer device used in this experiment with a linear gradient of the emitter is given in Figure 2a. For the device preparation, a combinatorial setup consisting of a movable mask sledge and a turnable substrate holder specially developed by us, the details of which were published earlier,¹⁰ was used. Three precleaned and oxygen plasma-treated (100 W, 999 s) ITO/glass substrates (dimension 2.54 cm × 7.6 cm, area 19.3 cm², ITO thickness: 110 nm, sheet resistance: 30 Ω/□) etched on one side 10.0 mm wide to avoid shorts between ITO and aluminum during contacting were placed together in a vacuum deposition chamber. As a first

Chem. Mater., Vol. 12, No. 10, 2000 3013

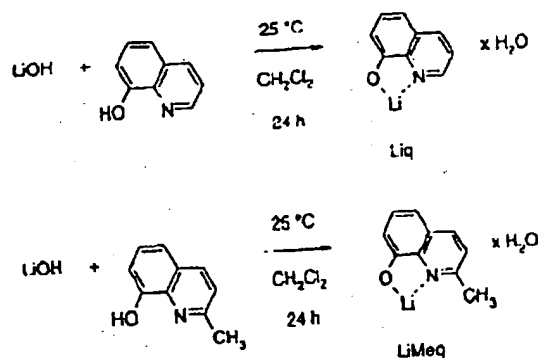


Figure 1. Scheme of synthesis of 8-hydroxyquinolinolitolithium (Liq) and 2-methyl-8-hydroxyquinolinolitolithium (LiMeq).

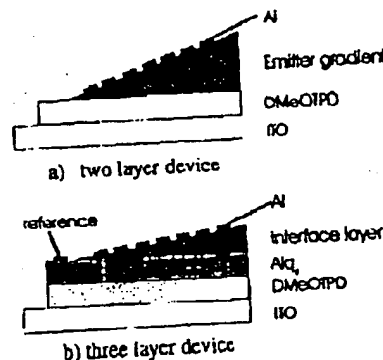


Figure 2. Schematic representation of (a) two-layer device configuration, ITO/DMeOTPD/emitter/Al, and (b) three-layer device configuration, ITO/DMeOTPD/Alq₃/interface layer/Al.

step, a 50 nm thick layer of DMeOTPD was vapor-deposited on all the substrates simultaneously. In a second step, linear gradients of Liq (30–150 nm), LiMeq (30–150 nm), and Alq₃ (30–100 nm) were deposited on the three different substrates one after another by the movable shadow mask technique without opening the vacuum chamber. Finally, aluminum was deposited as 24 stripes through a mask on each of the three substrates simultaneously. The active area of each device is 0.09 cm² (1.77 mm × 5 mm). The layer thickness for each device was obtained by calibrating the thickness gradient by measuring thicknesses at different points, for the measurement of thickness for very thin layers (less than 10 nm) was difficult with a surface profilometer and the calibration method gave exact values. All vapor depositions were carried out at a pressure of about 10⁻⁶ mbar.

Results and Discussion

It has been reported that some lithium metal complexes such as lithium tetra(8-hydroxyquinolinolato)-boron, 2-(2-hydroxyphenyl)benzoxazolinolitolithium, etc., can be used as efficient emitter materials in OLEDs.^{10,11} Although 8-hydroxyquinolinolitolithium has been tested as an Al/Alq₃ interface material, no systematic study of the lithium-quinolate complexes as emitter compounds and no comparison of these materials with the dielectric LiF as interface layers has been reported so far to the best of our knowledge. This comparison may answer the question if the lithium compounds improve OLED

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Table 1. Absorption, Fluorescence, Cyclic Voltammetry, and Thermal Data of Liq, LiMeq, Alq₃, and DMeOTPD

compound	abs (nm)	PL ^a (nm)	HOMO ^b (eV)	LUMO ^b (eV)	T _{5%} ^c (°C)
Liq	259, 365	485	-5.58	-3.15	360
LiMeq	259, 365	495	-5.49	-3.21	324
Alq ₃	410	520	-5.62	-2.58	
DMeO-TPD	360	433 (415)	-5.06	>-2.4	

^a Photoluminescence emission maximum wavelength. ^b From CV in acetonitrile vs Ag/AgNO₃ with ferrocene (Fc) as internal standard. ^c Temperature for 5% weight loss from TGA.

efficiency due to a doping effect or only due to an interface modification.

Synthesis. The synthetic scheme of preparation of the complexes Liq and LiMeq is shown in Figure 1. The details of synthesis are given in the Experimental Section. Kido and co-workers² have mentioned the synthesis of Liq from metal hydroxide and ligand without giving any details of procedure. Our attempt to prepare the complexes starting from LiOH and ligand in ethanol resulted in coordination of EtOH in the product. We also tried an alternative synthesis starting from *n*-butyllithium and ligand in THF, which also did not lead to the desired products. The synthesis in highly dried methylene chloride led to blue-green fluorescing quinolinolitolithium complexes. The exact structure of the complexes can be studied only by looking into the crystal structure, for these complexes take up water of crystallization depending on the conditions of synthesis and drying. In comparison to the classical lithium complexes, it can be assumed that lithium also forms complexes with possible structures such as [Liq]₂[Li(H₂O)₂]. The mass spectrometric analysis indicates the presence of fragments accounting for this structure. After drying, the mass spectroscopy analysis of Liq shows the peaks corresponding to fragments [Liq]₂[Li] (*m/z* = 302) and Liq (*m/z* = 151) and that of LiMeq shows the peaks corresponding to fragments [LiMeq]₂[Li] (*m/z* = 330) and LiMeq (*m/z* = 165) without any remaining water. The complexes show different elemental composition depending upon the degree of drying. A correct CHN analysis for fully dried complexes could not be obtained due to the high hygroscopic nature of the complexes. For practical purpose of discussion, we denote the synthesized compounds as Liq and LiMeq, respectively.

Optical, Electrochemical, and Thermal Properties. The absorption, fluorescence, and thermal properties of the complexes are summarized in Table 1. The thermal properties of the complexes were studied by thermogravimetric analysis (TGA). The Liq and LiMeq complexes as synthesized show 5% weight loss at 180 and 160 °C, respectively. The TGA curves show hints about the elimination of water of crystallization, and therefore the complexes were purified by drying at 200 °C in high vacuum. As a result, the thermal stability of the complexes increases but without any change in absorption spectra. The photoluminescence spectra of the complexes were measured in film obtained by vapor deposition of the compounds after drying at 200 °C in high vacuum. Both Liq and LiMeq show absorption maximum at about 260 nm and emission maximum at 485 nm. On comparison to Alq₃, the PL emission in lithium complexes is shifted to the blue region. The electrochemical stability and redox properties of the

complexes were studied by cyclic voltammetry. The redox potentials were measured at room temperature against Ag/AgNO₃ reference electrode and calibrated against ferrocene (Fc). Liq exhibits an oxidation at 0.84 V vs Ag/AgNO₃ (0.78 vs Fc) and a reduction at -1.59 V (-1.65 vs Fc). Assuming -4.8 eV as the highest occupied molecular orbital (HOMO) energy level for the Fc,¹² the HOMO and lowest unoccupied molecular orbital (LUMO) values for Liq are -5.58 and -3.15 eV, respectively. In a similar way the HOMO and LUMO values for LiMeq were detected as -5.49 eV (*E*_{ox} = 0.69 V vs Fc) and -3.21 eV (*E*_{red} = -1.59 V vs Fc), respectively. The oxidation is found to be irreversible whereas the reduction is reversible under our measuring conditions and scan rate from 50 to 500 mV/s. Thus, lithium complexes can be expected to have good electron injection properties due to these low reduction potentials. We observed a difference between the electrochemical band gap energy, *E*_{g(ec)} and the optical band gap, *E*_{g(opt)} in the case of lithium complexes. The *E*_{g(ec)}, which is the difference between HOMO and LUMO energy values obtained from CV, is comparable with the *E*_{g(opt)} if only the molecular species involved in electrochemistry and absorption are the same. In the case of Alq₃ this is the case and we observe a clear agreement between the measured *E*_{g(ec)} (3.04 eV = 408 nm) and *E*_{g(opt)} (3.02 eV = 410 nm). In the case of Liq and LiMeq the actual molecular species are [Liq]₂[Li]⁺ and [LiMeq]₂[Li]⁺, respectively. These compounds show the oxidation and reduction of the different ionic species present in the molecule and therefore the *E*_{g(ec)} calculated from these complexes are different from the *E*_{g(opt)}. The band gap energy of Liq and LiMeq should be taken from the absorption spectra and it corresponds to 365 nm = 3.40 eV.

OLEDs with Lithium Complexes as Emitters. In a first experiment the electron injection/transport and emission properties of the complexes were studied in detail by using lithium complexes as emitter compounds in OLEDs. The lithium complexes were tested and compared with Alq₃ in two-layer devices with the configuration ITO/DMeOTPD/Liq or LiMeq or Alq₃/Al as described in the Experimental Section. In this way, Liq, LiMeq, and Alq₃ devices with the same thickness of DMeOTPD and different emitter layer thicknesses were prepared in one single experiment under same conditions. This enables us to optimize the power efficiency, photometric efficiency, and current-voltage characteristics for each emitter material and to compare their properties. As an example, the thickness optimization and the dependence of efficiency on the thickness of the Liq layer will be described in detail. Figure 3 shows the characteristics of 10 different devices with Liq thickness varying from 44 to 128 nm. As expected, there is an optimum thickness of Liq for maximum efficiency and luminance for a constant layer thickness of DMeOTPD.⁸ The efficiency of the devices with Liq thickness between 66 and 96 nm is considerably high and a maximum efficiency of 1.46 cd/A (at 31 mA/cm²) is attained for a device with Liq thickness of 86 nm (Figure 3b). The same device shows a maximum luminance of 1642 cd/m² at 193 mA/cm². A similar behavior

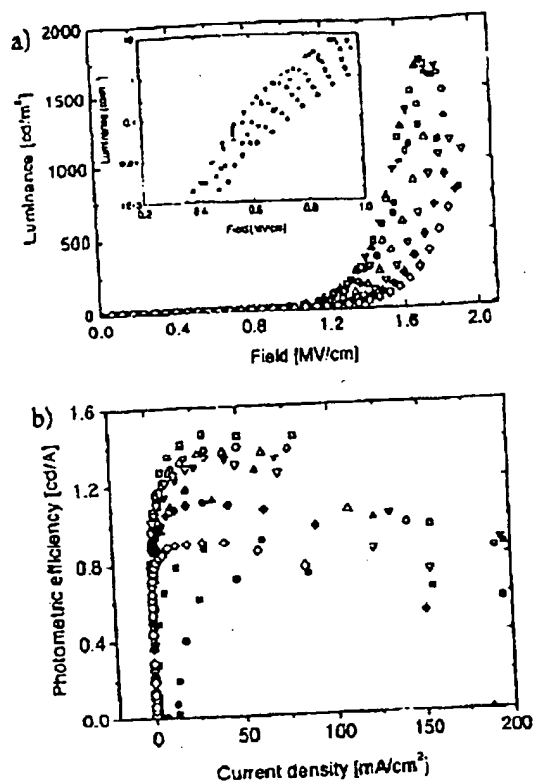


Figure 3. Plots of (a) luminance as a function of field and (b) photometric efficiency vs current density for the devices ITO/DMeOTPD (50 nm)/Liq gradient (30–150 nm)/AL. Liq thickness: (■) 44 nm, (●) 54 nm, (▲) 68 nm, (▼) 77 nm, (□) 86 nm, (○) 96 nm, (△) 105 nm, (▽) 114 nm, (◇) 124 nm, (○) 128 nm.

of thickness dependence of power efficiency is also observed. A maximum power efficiency of 0.08 cd/W (at 6.6 mA/cm²) was achieved for the same device with 86 nm Liq thickness. Figure 3a shows the Liq thickness dependence of electroluminescence onset, which is similar to the dependence of the photometric efficiency and power efficiency on Liq thickness. The onset decreases with increasing Liq thickness from 44 to 86 nm to reach an optimum value of 0.36 MV/cm \approx 4 V (for 0.001 cd/m²). Further increase in Liq layer thickness leads to an increase in onset voltage. The inset in Figure 3a reveals this clearly.

In the case of LiMeq devices (not shown), the device with 76 nm LiMeq shows the maximum photometric efficiency of 1.13 cd/A (at 41 mA/cm²) and maximum luminance of 1236 cd/m² (at 164 mA/cm²). The maximum power efficiency and onset voltage for this device are 0.05 cd/W (at 35 mA/cm²) and 0.55 MV/cm \approx 7 V (for 0.001 cd/m²), respectively. The thickness optimization in Alq₃ devices results in a maximum luminance of 5653 cd/m² (at 217 mA/cm²) and a maximum photometric efficiency of 4.6 cd/A (at 47 mA/cm²) for the device with 66 nm Alq₃ layer thickness. This optimum device exhibits a maximum power efficiency of 0.37 cd/W (at 9 mA/cm²) and an onset voltage of 3 V (0.24 MV/cm) for 0.001 cd/m². These values are appreciably good taking into consideration that the devices have no additional interface layers such as CuPc for balanced charge injection as reported in the literature.^{13,6} The overall

comparison of the device characteristics for the three optimized devices with Liq, LiMeq, and Alq₃ as emitter is given in Table 2 and the current voltage characteristics of the three optimized devices are compared in Figure 4. It is obvious that the complexes Liq and LiMeq are both good emitter materials exhibiting appreciably high luminance and efficiency and low onset voltages. However, an optimized Alq₃ device exhibits better device characteristics than do Liq and LiMeq devices (see Figure 4a). For the optimized devices, the increase in onset voltage from 3 V (0.24 MV/cm) for the Alq₃ device to 4 V (0.36 MV/cm) for the Liq device and 7 V (0.55 MV/cm) for the LiMeq device (see Figure 4b) can be attributed to the difference in the electron injection and electron transport properties of the different emitter complexes. The LUMO values determined from cyclic voltammetry for Liq, LiMeq, and Alq₃ are -3.15, -3.21, and -2.58 eV, respectively. The electron injection from aluminum into the emitter should be favored in the order of minimum barrier energy. According to the measured LUMO values, the electron injection should be easier into LiMeq and Liq than into Alq₃. This is in contrast to the observed onset values for the devices using the three complexes as emitter. In literature it is described that the actual electron injection is favored or disfavored according to the interface energy level modification between cathode and emitter.^{13–15} Seki and co-workers¹³ have observed different energy level modifications for Al/Alq₃, Al/LiF, and Al/LiF/Alq₃ interfaces. Moreover, they found that the deposition of Alq₃ on aluminum induces an extra occupied state above the HOMO, suggesting a strong chemical interaction between Al and Alq₃ and also that the insertion of LiF eliminated these states. The Al/Liq and Al/LiMeq interfaces have not yet been examined for possible electronic energy level modification. Therefore, it is not possible to account for the observed behavior of these complexes with respect to electron injection from aluminum. But it can be supposed that the interface energy level modification in Al/Alq₃ should be better than in Al/Liq and Al/LiMeq interfaces to explain the better electron injection at the Al/Alq₃ interface. Additionally, the whole picture may be complicated through possible chemical reactions and interdiffusion effects at the metal complex/HTL interface, which may be entirely different for Li quinolates and Alq₃.

The EL spectra of lithium quinolate devices are blue-shifted compared to that from an Alq₃ device. The CIE coordinates for the most efficient Liq and LiMeq devices were measured to be $x = 0.27$, $y = 0.39$ and $x = 0.24$, $y = 0.39$, respectively, whereas that for Alq₃ are found to be $x = 0.320$, $y = 0.559$. The electroluminescence (EL) spectrum of Alq₃ devices resembles the photoluminescence (PL) spectrum of Alq₃. But in the case of Liq and LiMeq devices, the EL spectra differ slightly from the corresponding PL spectra of vapor-deposited Liq and LiMeq films, respectively. In both cases, there is neither voltage nor thickness tuning of EL. It means that there

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Table 2. Characteristic Data of the Optimized Devices: ITO/DMeOTPD (50 nm)/LiQ (88 nm)/Al (60 nm)/LiQ (76 nm)/Al, and ITO/DMeOTPD (50 nm)/Alq₃ (66 nm)/Al

optimized device ITO/HTL/EM/AL	luminance (cd/m ²) at 10 mA/cm ²	current density (mA/cm ²) at 100 cd/m ²	onset voltage (V) at 0.001 cd/m ²	max brightness (cd/m ²)
LiQ (88 nm)	122	8	4	1642
LiMeq (76 nm)	100	10	7	1236
Alq ₃ (66 nm)	404	3	2	5653

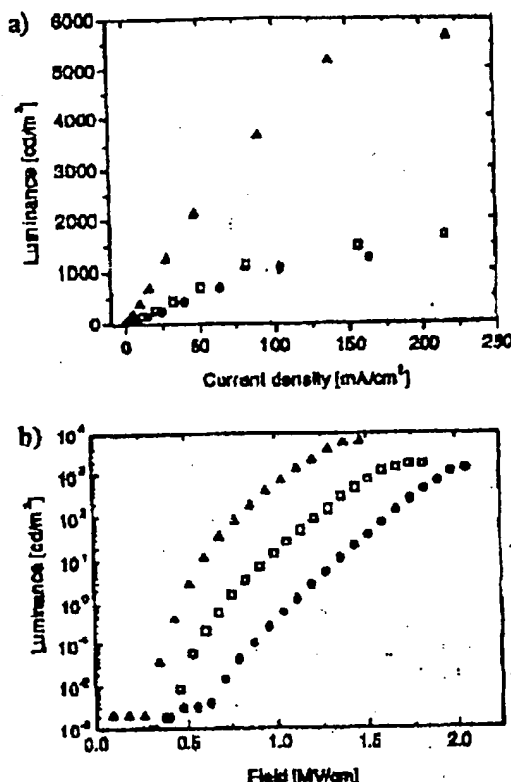


Figure 4. Luminance as a function of (a) current density and (b) field for the three optimized devices: (○) ITO/DMeOTPD (50 nm)/LiQ (88 nm)/Al, (●) ITO/DMeOTPD (50 nm)/LiMeq (76 nm)/Al, and (▲) ITO/DMeOTPD (50 nm)/Alq₃ (66 nm)/Al.

is no bathochromic and no hypsochromic shift of the EL spectra with variation of either bias or organic layer thickness. To understand the origin of the EL spectra and the emitting species in LiQ and LiMeq devices, the PL spectra of vapor-deposited films of DMeOTPD and LiQ or LiMeq (both complexes after drying at 200 °C) were compared with the corresponding EL spectra. The PL spectra of LiQ and LiMeq are similar with a λ_{max} at 486 nm, whereas both the devices exhibit EL spectra with λ_{max} of about 495 nm and a shoulder at 415 nm. It can be concluded that the EL emission (except the shoulder at 415 nm) does not originate from DMeOTPD, for it has PL λ_{max} values of 414 and 433 nm. The red shift in EL spectra of about 10 nm compared to the respective PL spectrum of the emitter may be due to the formation of exciplex at the HTL/emitter interface.

Shirota and co-workers¹⁶ have observed the formation of exciplex at hole transport (HTL)/emitter (EM) interface in devices by using an HTL with low oxidation

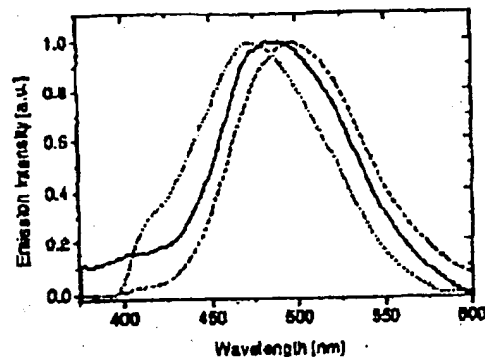


Figure 5. Comparison of photoluminescence (PL) and electroluminescence (EL) spectra: (—) PL of vapor-deposited LiQ (dried at 200 °C in HV film); (---) PL of 1:1 mixture of DMeOTPD and LiQ in film; (···) EL of device ITO/DMeOTPD (50 nm)/LiQ (88 nm)/Al.

potential like m-MTDATA and an emitter Alq₃, respectively. The formation of exciplex between DMeOTPD and LiQ or LiMeq may be favored by the low LUMO values of these emitters and the low oxidation potential of DMeOTPD (see Table 1). Alq₃ has comparatively a high LUMO value and therefore no exciplex formation is observed at the interface DMeOTPD/Alq₃. To observe an exciplex emission from HTL/Alq₃, a much lower oxidation potential for the HTL is required and it is reported in the case of m-MTDATA. In the case of exciplex formation between HTL and EM, the EL spectra should be in good agreement with the PL spectra of an equimolar mixture of HTL and EM. To examine such a possibility in our case, we compared the PL emission of a film prepared from a 1:1 mixture of LiQ and DMeOTPD with the EL spectra of the device ITO/DMeOTPD (50 nm)/LiQ (88 nm)/Al (see Figure 5). The PL λ_{max} of the mixture is at 475 nm with a shoulder at 415 nm.

This indicates that the EL emission at 495 nm lies more closely to the PL spectra of the vapor-deposited film of pure lithium complex than to that of the 1:1 mixture. Thus, we do not observe any clear evidence for the exciplex emission. The spectral differences between PL and EL can also not be ascribed to a microcavity effect due to varying thicknesses of the organic layers, for the EL spectrum remains the same for all thicknesses of lithium complex. The observed shoulder at 415 nm in the EL emission may be attributed to the exciton formation in HTL at the interface. This arises by possible interlayer diffusion of lithium quinolates into HTL, resulting in an increase of the interface region. The interlayer diffusion can be studied by X-ray photoelectron spectroscopy (XPS or ESCA), which is under consideration.

Lithium–Quinolate Interface Layers in OLEDs. In a second experiment the effect of LiQ and LiMeq as interface layers between Alq₃ and aluminum in ITO/

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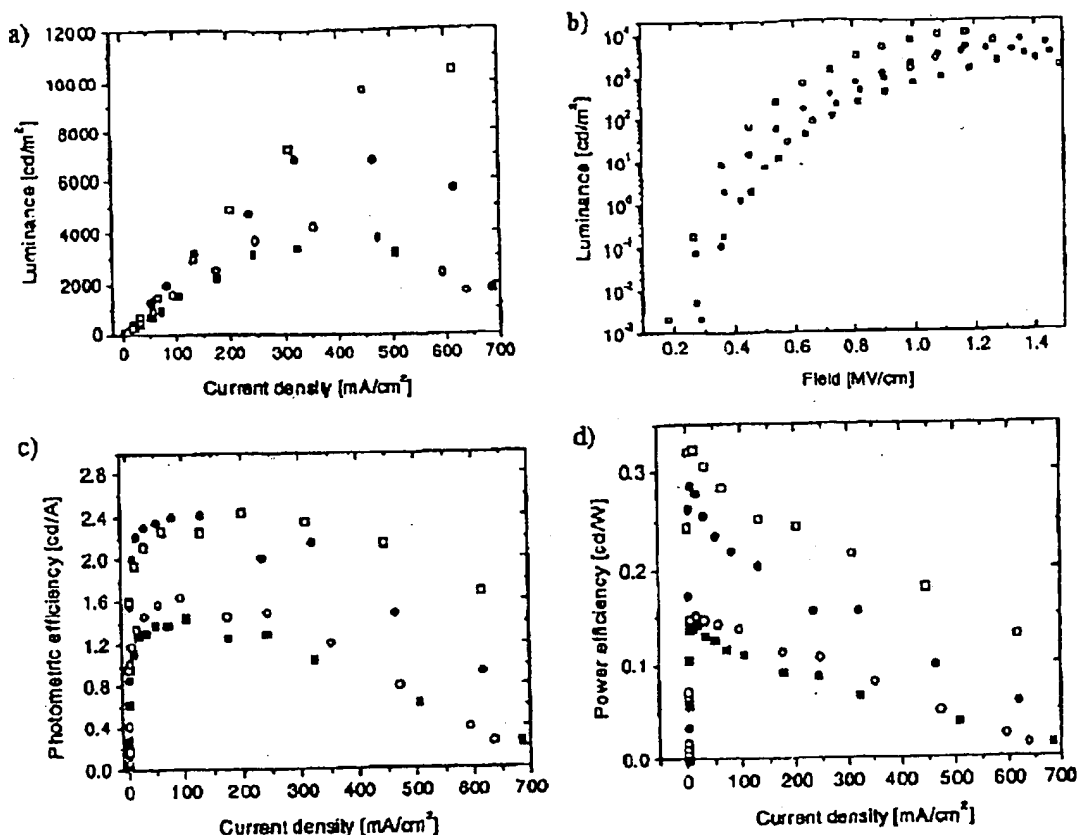


Figure 5. (a) Efficiency plots of luminance vs current density; (b) onset plots of luminance vs field; (c) photometric efficiency against current density, and (d) power efficiency vs current density of the four devices: (■) device 1, ITO/DMeOTPD (50 nm)/Alq₃ (60 nm)/Al [reference two layer]; (●) device 2, ITO/DMeOTPD (50 nm)/Alq₃ (60 nm)/LiQ (0.6 nm)/Al; (□) device 3, ITO/DMeOTPD (50 nm)/Alq₃ (60 nm)/LiMeq (1.1 nm)/Al; and (○) device 4, ITO/DMeOTPD (50 nm)/Alq₃ (71 nm)/Al.

DMeOTPD/Alq₃/Al devices was examined. Similar to the first experiment, three precleaned ITO substrates were simultaneously coated with a constant layer thickness of 50 nm of DMeOTPD. In a second step, two of the substrates were deposited with 60 nm of Alq₃ layer and the third substrate with a gradient of 0–80 nm of Alq₃. The latter device gives information about the optimized DMeOTPD/Alq₃ device with optimum Alq₃ thickness (see Figure 2a for the device configuration). Finally, the two substrates with constant thickness of Alq₃ layer were deposited with gradients (0–40 nm) of Liq and LiMeq, respectively, after leaving 10 mm broad sector. This area is to be used for the preparation of a reference two-layer device, ITO/DMeOTPD (50 nm)/Alq₃ (60 nm)/Al without any interface modification (see Figure 2b). In this way, comparable ITO/DMeOTPD/Alq₃/Al devices with and without an interface layer were prepared to study the effect of an additional interface layer and to compare with the efficiency of an optimized two-layer device.

The efficiency plots of luminance vs current density for the reference two-layer device ITO/DMeOTPD (50 nm)/Alq₃ (60 nm)/Al compared with those for devices with different thicknesses of additional Liq or LiMeq interface layer show that only very thin interface layer improves the device characteristics (not shown). In the case of Liq, an interface layer of 0.6 nm improves the maximum luminance to 6922 cd/m² (at 322 mA/cm²)

compared to the reference two-layer device which exhibits maximum luminance of 3400 cd/m² at 320 mA/cm². In a similar way, a 1.1 nm thick LiMeq interface layer leads to an improvement of the maximum luminance to 9700 cd/m² (at 444 mA/cm²). In terms of photometric efficiency at 100 mA/cm² the improvements with thin Liq or LiMeq interface layers are 2.44 and 2.35 cd/A, respectively, compared to the two-layer device with an efficiency of 1.39 cd/A.

Within the same experiment the substrate with Alq₃ thickness gradient from 0 to 80 nm on top of 50 nm DMeOTPD revealed that ITO/DMeOTPD (50 nm)/Alq₃ (71 nm)/Al was the most efficient device. To compare the effect of an additional Liq or LiMeq interface layer in a two-layer ITO/DMeOTPD/Alq₃/Al device with that of the optimized two-layer device with optimum layer thickness of 71 nm Alq₃, the characteristics of the following devices are compared in Figure 6: device 1, ITO/DMeOTPD (50 nm)/Alq₃ (60 nm)/Al [reference device]; device 2, ITO/DMeOTPD (50 nm)/Alq₃ (60 nm)/Liq (0.6 nm)/Al; device 3, ITO/DMeOTPD (50 nm)/Alq₃ (60 nm)/LiMeq (1.1 nm)/Al; and device 4, ITO/DMeOTPD (50 nm)/Alq₃ (71 nm)/Al [optimized device].

Figure 6a shows that the efficiency of the reference device (device 1) is similar to that of the optimized device 4 with an optimum thickness of Alq₃ layer of 71 nm. The maximum photometric efficiencies of devices 1 and 4 are 1.39 cd/A (at 100 mA/cm²) and 1.65 cd/A (at

100 mA/cm²), respectively. Both devices 2 and 3 with very thin additional Liq or LiMeq layers show a considerable improvement in photometric efficiency with corresponding values of 2.44 cd/A (at 100 mA/cm²) and 2.35 cd/A (at 100 mA/cm²) respectively (see Figure 6c). A similar improvement in power efficiency can be observed for devices with interface modification (see Figure 6d). Further, there is a slight improvement in the onset voltages for devices 2 and 3 compared to both of the two-layer devices 1 and 4 (Figure 6b). The improvement in device characteristics observed here is in close agreement with the results obtained by Kido and co-workers,² who used various alkaline metal complexes as interface layers in a TPD/Alq₃ device. These authors assume that a central metal ion in these metal complexes is reduced to the low work function metal by the reaction between the complexes and thermally activated aluminum, which leads to the formation of a 8-hydroxyquinolate radical anion at the interface, resulting in improvement of electron injection from aluminum cathode.

Comparison of Lithium Complexes with LiF as Interface Material. The use of a bilayer consisting of ultrathin dielectric layers of LiF, MgO, etc., between Alq₃ and aluminum is also found to improve device characteristics considerably, whereas a dielectric like GeO₂ worsens the device characteristics of highly optimized TPD/Alq₃ devices.¹ Hung et al.¹ attribute the improvements in device characteristics to band bending of the organic layer in contact with the dielectric. This argument cannot explain the effect of the GeO₂ interface layer. To examine and understand the real reason for device improvement due to dielectrics or with lithium-quinolate complexes as interface layer, we prepared three sets of devices with the following structures: device A, ITO/DMeOTPD (40 nm)/Alq₃ (65 nm)/Liq gradient (0–30 nm)/Al; device B, ITO/DMeOTPD (40 nm)/Alq₃ (65 nm)/LiMeq gradient (0–30 nm)/Al; and device C, ITO/DMeOTPD (40 nm)/Alq₃ (65 nm)/LiF gradient (0–30 nm)/Al. We compared the device characteristics with the two-layer reference device ITO/DMeOTPD (40 nm)/Alq₃ (65 nm)/Al in one single experiment. The devices A, B, and C have the configuration as shown in Figure 2b. In all three devices A, B, and C the maximum improvement in efficiency and onset voltage is observed on depositing a thin layer (about 0.4 nm) of the interface layer independent of the nature of the interface material. In all cases, the device characteristics are worsened if the thickness of the interface layer is greater than about 1.5 nm. Figure 7 depicts the current-voltage and luminance-current density plots of the devices A, B, and C with 0.4 nm of different interface layers and the two-layer reference device. The reference device without any interface layer requires 16 V to generate a current density of 100 mA/cm². With the introduction of an interface layer the required voltages are decreased in the order Liq (14 V) > LiF (13 V) > LiMeq (12 V) (Figure 7a). The light output is directly proportional to the injected current and the slope of the curves in Figure 7b, which represent the EL efficiency improvements in the same order as onset voltage. The EL output for the devices A, B, and C for an injected current of 100 mA/cm² is approximately the same (1800 cd/m²) compared to the reference

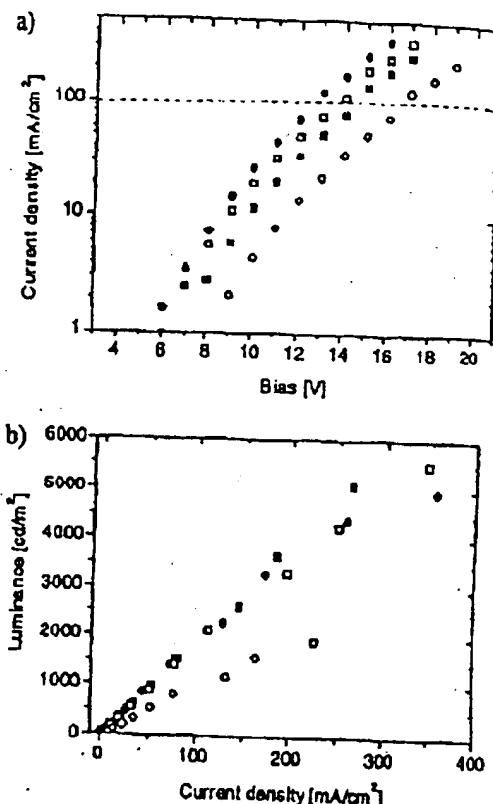


Figure 7. (a) Current-voltage characteristics and (b) efficiency plots of light output in cd/m² vs injected current density for the four types of devices: (○) ITO/DMeOTPD (40 nm)/Alq₃ (65 nm)/Al (reference two-layer); (□) ITO/DMeOTPD (40 nm)/Alq₃ (65 nm)/Liq (0.4 nm)/Al; (●) ITO/DMeOTPD (40 nm)/Alq₃ (65 nm)/LiMeq (0.4 nm)/Al; and (■) ITO/DMeOTPD (40 nm)/Alq₃ (65 nm)/LiF (0.4 nm)/Al.

device with 960 cd/m². The corresponding photometric efficiencies are 2.0 and 1.0 cd/A, respectively.

The observed improvement in devices A, B, and C is of a similar nature and is independent of the chemical nature of the interface material, and in all these three cases the central atom is a low work function metal like lithium. This means that the mechanism of interface modification seems to be the same for an organic electron injection/transport material like lithium-quinolate complex as well as for a dielectric LiF. LiF is a superior insulating material with a very high band gap energy of 13.6–14.5 eV,¹⁵ whereas the lithium complexes have band gap energies of about 3.4 eV and LUMO values of about -3.2 eV. The concept of tunneling injection through a thin dielectric cannot be applied to explain the improvement of device characteristics with such entirely electronically different interface materials and also the observed worsening effect with GeO₂ as interface layer as reported earlier.¹ A common characteristic for the interface materials such as MgO, LiF, Liq, and LiMeq is that the central atom is an electropositive low work function metal whereas in GeO₂, the metal atom Ge has a high work function of about 5 eV. The concept of reduction of the interface material by the thermally activated aluminum leading to dopable metals such as Li and Mg in the former case put forward by Kido and co-workers^{2,3} explains satis-

factorily the observed device improvements with LiF, MgO and lithium complexes. It also explains the impossibility of the formation of germanium metal and thus a doping effect in the latter case. But Saki and co-workers¹² have shown that the injection barrier at the Alq₃/Al interface is considerably modified by a shift of the vacuum zero energy level due to various interface layers. Therefore, it is worthwhile to examine the exact interface modification by using XPS measurements before coming to a conclusion regarding the mechanism of interface modification.

Conclusions

To conclude, we synthesized two lithium-quinolate complexes as emitter molecules and tested them in OLEDs with DMeOTPD as HTL. The device parameters were efficiently optimized by a combinatorial approach in a fast manner. Both Liq and LiMeq are efficient emitter molecules with good electron injection and electron transport properties. The EL emission in Li quinolates is bathochromically shifted compared to

their PL spectra. No clear evidence is observed for exciplex emission from the emitter/HTL interface. On comparison with Alq₃, the efficiencies of Li quinolate devices are low. Very thin interface layers of lithium complexes improved the device performance of the two-layer DMeOTPD/Alq₃ device considerably. The improvement with lithium complexes as interface layers is similar to that of a dielectric like LiF, which suggests that the concept of tunneling injection through a thin insulation layer perhaps may not be valid and the concept of doping through a reduced low work function metal explains the general improvement observed independent of the chemical nature of the interface material.

Acknowledgment. Financial support from SPB 481-Complex macromolecular and hybrid systems in internal and external fields (Projects A6 and B4) and Fonds der chemischen Industrie - BMBF (C. Schmitz) is kindly acknowledged.

CM0010248